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(54) **Liquid cleaning products.**

(57) A non-aqueous liquid cleaning composition comprising a non-aqueous phase with dispersed particles comprising a carrier material and dye material associated thereto wherein the carrier-dye particles have a certain D(3,2) particle size; a method for preparing the carrier-dye particles; and method for preparing the non-aqueous liquid with carrier-dye particles.

**EP 0 635 569 A2**

TECHNICAL FIELD

The present invention relates to substantially non-aqueous liquid cleaning products, especially detergent compositions and to a method of preparing such non-aqueous liquid cleaning products. Non-aqueous liquid cleaning products are those containing little or no water.

PRIOR ART & BACKGROUND

Non-aqueous liquid detergent compositions are known in the art and have been described in quite a number of patent publications, e.g. in US-A-4,316,812, US-A-4,874,537 and EP-A-0,484,095. Generally, the free water content of non-aqueous liquid detergent products is less than 5% by weight, preferably less than 3% by weight, more preferably less than 2% by weight, most preferably substantially nil. Non-aqueous liquid detergent compositions provide a way of concentrating liquid detergents without giving in on washing performance.

Non-aqueous liquid detergent compositions normally comprise a non-aqueous liquid phase having incorporated therein as dispersion, solution or combination thereof, the usual detergent components and adjuncts depending on the purpose of use, primarily surfactants and builders.

The liquid phase often comprises a nonionic surfactant as major component, which apart from acting as carrier liquid for the other detergent components, usually and preferably also has detergent-active properties, thereby acting wholly or in part as the surfactant ingredient.

Adjuncts such as dyes are important ingredients incorporated in products, usually in small amounts to provide for certain desired properties. Dye may be included in non-aqueous liquids to improve the product appearance, as a warning to consumers for toxic ingredients and/or to mask consumer-disliked colours of detergent ingredients.

GB-A-1,303,810 discloses clear liquid detergent compositions with a transparent aqueous or non-aqueous base comprising particles that are visually distinct and have a diameter size of at least 0.5 mm. The formulation of these liquids is restricted as they must have a transparent liquid base and the suspending power of the liquid must be sufficiently high in order to stably suspend the particles with the large particle size, which may cause the product to have a high viscosity.

GB-A-2,194,793 discloses liquid detergent compositions having an aqueous base that comprise high electrolyte levels and suspended particles having a particle size of from 1 to 2000  $\mu\text{m}$ , preferably up to 300  $\mu\text{m}$ . The aqueous liquids are prepared to have a mottled or speckled coloration appearance by using a pigment material and a carrier material for the suspended particles that are substantially insoluble and non-dispersible in the suspending aqueous liquid. To prepare chemically stable formulation according to this reference on aqueous liquids it is not only required to select specific insoluble pigment and carrier materials that have to be stable in the aqueous liquid over time, but it is also necessary to incorporate high levels of electrolyte in the aqueous base, i.e. at least up to its solubility limit.

It is sometimes difficult to satisfactorily incorporate a dye in non-aqueous liquids. Non-aqueous liquid cleaning compositions are among the most concentrated products in the art and the number of interactions between the ingredients of such products makes it in particular difficult to prepare compositions that are chemically stable, especially upon storage. This is not only true as compared with diluted aqueous liquids but also with powdered products in which components have a more or less fixed position in the product.

Frequently non-aqueous liquids comprising dye suffer from discolouring, i.e. fading and/or disappearance of the colour which leads to a worse product appearance, decreased effect of the warning function and less or no masking of consumer-disliked colours of ingredients of the non-aqueous liquid.

It is an object of the present invention to improve the product appearance, to improve the colour warning system and/or to improve masking of consumer-disliked colours of detergent ingredients of non-aqueous liquids and/or to overcome fading of the colour upon storage.

SUMMARY OF THE INVENTION

In its broadest embodiment, the present invention provides a non-aqueous liquid cleaning composition comprising a non-aqueous phase with dispersed particles comprising a carrier material and dye material associated thereto wherein the particles have a D(3,2) particle size of from 50  $\mu\text{m}$  to less than 500  $\mu\text{m}$ .

A preferred embodiment of the invention provides a non-aqueous liquid comprising a non-aqueous phase and dispersed particles wherein the particles comprise a biopolymer as carrier material, and dye associated thereto.

A further embodiment of the invention provides a non-aqueous liquid comprising a non-aqueous phase and dispersed particles comprising a carrier material and dye material associated thereto, wherein the composition further comprises a bleach material.

5 A further embodiment of the invention provides a method of preparing a non-aqueous liquid cleaning composition having a non-aqueous phase with dispersed particles, said method comprising dispersing particles, comprising carrier material and dye material associated thereto, in the non-aqueous phase.

A further embodiment of the present invention provides a method of preparing a particle, comprising carrier material and dye material associated thereto, and suitable for use in a non-aqueous liquid cleaning composition, said method comprising dissolving of a biopolymer material in water, evaporating the water to  
10 an amount of lower than 15% by weight of the resulting material and before, during or after the evaporation step adding of dye material and subjecting the resulting material to milling and/or sieving.

#### DETAILED DESCRIPTION OF THE INVENTION

15 The presently claimed invention not only overcomes colour fading of the dispersed particles but is believed also to provide a product with consumer preferred appearance as the resulting non-aqueous liquid will comprise coloured speckles suspended in the non-aqueous liquid phase.

Applicants have further surprisingly found that dispersion of the particles with carrier material and dye material wherein the size of the particles is not smaller than 50µm, in particular smaller than 90µm, more  
20 particularly smaller than 100µm, leads to a better distinction of the particles from the rest of the formulation, the so-called non-aqueous base, which is the non-aqueous liquid cleaning composition without the dispersed particles of carrier and dye material. Preferably not more than 25% by weight of the particles, more preferably not more than 10% by weight, most preferably not more than 5% by weight of the particles have a size smaller than 50µm, more preferably smaller than 90µm, more preferably smaller than 100µm. If  
25 smaller particles are used then the colour of the base of the liquid colour tends to become greyish, resulting in the dispersed particles not being distinct anymore, which may deteriorate one or more of the above mentioned effects.

Furthermore, the use of dye material for particles enables preparation of non-aqueous cleaning compositions that can be formulated more flexibly, e.g. masking the undesired colours of other ingredients.

30 Presence of a bleach system in the non-aqueous liquid cleaning composition of the invention, preferably a low temperature bleach system, i.e. a bleach system that is effective at temperatures of 60 °C or lower, is a preferred embodiment of the invention. Without wishing to be bound by any theory, it is thought that the bleach system in the non-aqueous liquid cleaning composition of the invention will react with the dye material as soon as the dye and bleach are released in the wash liquor and this consequently  
35 prevents the dye from depositing on the material to be washed.

#### DISPERSED PARTICLES

40 The dispersed particles according to the invention comprise carrier material and dye material. The dye material can be present on the outside and/or in the inside of the particle.

In both case it is believed that association of dye to the carrier material reduces interaction of dye with other ingredients present in the non-aqueous liquids. It is preferred that the dye is present inside the particle to avoid substantially all interactions with other ingredients. This also reduces diffusion of the dye into the non-aqueous liquid phase upon storage. Particles with dye present on the outside of the particle,  
45 e.g. in a layer, can however be preferred for processing reasons, as manufacturing of such particles can take place at low costs, e.g. by simply rolling carrier material in a bed of dye material or by spaying the dye material on the carrier material.

The dye material can be associated to the carrier material by way of physical, e.g. Van der Waals forces or hydrogen bonding and also by way of chemical association, such as complexing and covalent  
50 bonding.

Preferably the particle size D(3,2) of the dispersed particles is at least 50µm, more preferably at least 100µm, most preferably at least 150µm and particularly preferred at least 180µm. Preferably the particles have a particle size of less than 500µm, preferably less than 300 µm, most preferably at most 250µm. For the purpose of the present invention references to the D(3,2) average particle diameter refer to the D(3,2)  
55 particle size, which is the average surface weighted, volume/weight mean diameter calculated as described by M. Alderliesten, Anal. Proc. Vol. 21, May, 1984, 167 to 172. The particle size can for example be determined with a Malvern Mastersizer and preferably by using a sweep sieve.

Preferably the dispersed particles are present in the non-aqueous phase in a volume fraction of from 0.1 to 5.0% V/V of the total non-aqueous liquid cleaning composition, more preferably 0.3 to 3.0% V/V, most preferably 0.5 to 2.0% V/V.

The colour of the non-aqueous base as well as of the dispersed particles with carrier and dye material can be expressed in L, A and/or B values. The L, A and B colour values are well-known in the art (ex CIE LAB, 1976). The values represent colour intensity units. For the purpose of this invention the values for L, A and B are determined by using a Chromameter (ex Minolta) of the CR series, i.e. CR-300, CR-310, CR-321, CR-331 or CT-310 of which the CT-310 and in particular the CR-300 are preferred. The manual of e.g. CR-310 contain a clear explanation as to the definition of the L, A and B colour values.

The L, A and B values for the non-aqueous base can be determined by measuring the L, A and B value of the non-aqueous base alone, i.e. the non-aqueous liquid cleaning composition without the dispersed particles comprising carrier and dye material.

Preferably, the dispersed particles with carrier and dye material are measured in the non-aqueous phase, but for practical purposes the value can also be determined of the particles per se.

It is preferred that the difference between the intensity of the dispersed particles with carrier and dye material and the intensity of the non-aqueous base (the delta value) is such that the L, A and/or B units show a difference of 10 units or more, preferably 15 units or more, more preferably 20 units or more, i.e. the delta value is preferably higher than 10 and/or lower than -10, more preferably higher than 15 and/or lower than 15, most preferably higher than 20 and/or lower than -20.

The dispersed particles comprising carrier and dye material can have high as well as low density. Although still dependent on the particles size, for reasons of physical stability it is preferred that the density of the dispersed particle is at least 0.1 mg/l, more preferably at least 0.8 mg/l and most preferably at least 1.0 mg/l. Preferably the density is at most 1.8 g/ml, more preferably at most 1.5 g/ml, most preferably at most 1.3 g/ml.

The dispersed particles may be used in the composition at levels of up to 80% by weight of the composition, preferably of up to 40% by weight of the composition, more preferably of up to 20% by weight of the composition, particularly preferred of up to 10% by weight of the composition. The lower level will generally be about 0.01% by weight of the composition, preferably 0.1% by weight of the composition, more preferably 0.2% by weight of the composition and most preferably 0.5% by weight of the composition.

#### DYE MATERIAL

For the purpose of the present invention the term dye material also covers pigment material.

Preferably the dye material is selected from red, orange, yellow, green, blue dyes and mixtures thereof such as pink. More preferably dyes are selected that have a colour selected from blue, green and pink.

Preferably the dye is chemically and physically stable in association with the specific carrier material in the non-aqueous liquid and preferably the dye does not cause spotting on articles in the wash cycle.

Dye material from any of the established dye classes can be selected. Preferably the dye is selected from Disperse, Acid, Reactive, Direct, Sulphur, VAT and Azo type dyes. Pigments can be applied in a similar manner. Examples of Disperse dyes are Dispersed Blue 69-0007 ex BASF (CI pigment Blue 15:1 CI constitution number 74160) and Patent Blue V80 (CI 42051).

Preferably the dye material is included in the product at levels of at least  $10^{-6}$ % by weight of the composition, more preferably at least  $10^{-4}$ % by weight of the composition, most preferably at least  $10^{-2}$ % by weight of the composition. Preferably the level is at most 2% by weight of the composition, more preferably at most 1% by weight of the composition, more preferably at most 0.75% by weight of the composition. The dye material can for example be included in levels of 0.0075% or of 0.025% by weight of the composition.

Preferably, the level of dye by weight of the dispersed particle is at least 0.0001%, more preferred at least 0.001, most preferred at least 0.01% by weight; the level is preferably at most 5%, more preferably at most 1%, most preferably at most 0.5% by weight.

#### CARRIER MATERIAL

Carrier material can be selected from a wide range of material to which the dye is associated. It is however preferred that the carrier material does not affect the dye, i.e. is inert to the dye material. Such carrier material can be selected from bleach, builder, clay, abrasive, enzyme and biopolymer material and mixtures thereof. Preferably, the carrier material comprises biopolymer material and the biopolymer material

usable in the present invention may be selected from a wide variety of biopolymers.

An advantage of the use of the biopolymers is their natural source, which makes their use environmentally acceptable. Preferred biopolymers are polysaccharides and polypeptides. Examples of such biopolymers include starch, gelatin, pectin, casein, amylopectin (corn or potato) and custard. Examples of starches are potato starch, wheat starch, corn starch, cereal starch, rice starch, tapioca starch and other modifications thereof, such as depolymerized starch. Other examples of suitable biopolymer materials are amylose, substituted cellulose (tylose), whey proteins and zein, hemicelluloses, pentosans, chitin derived from shellfish, seaweed extracts such as alginates, carrageenans, agar and furcelleran, pectines from plants, and also gums from different sources such as gum arabic, arabic kary, tragacanth, locust bean, guar and xanthan.

If a biopolymer is used, a preferred method for preparing the particle is as follows. A biopolymer material is dissolved in water, whereafter the water is allowed to evaporate which leaves a solid material having a water content of not more than about 15% by weight, preferably less than 12% by weight, more preferably less than 10% by weight. Optionally, the resulting material is subjected to milling and/or sieving.

Preferably, the biopolymer material is mixed with water at a weight ratio of biopolymer material to water of from 1:99 to 35:65, preferably from 2:98 to 30:70, more preferably from 3:97 to 25:75, and thereafter heated as desired, e.g. by short boiling of the mixture to cause dissolution of the biopolymer material in the water.

The solution is then left to stand so as to allow the water to evaporate. The temperature at which evaporation takes place will preferably be lower than 80 °C, more preferably less than 50 °C. The best results are obtained between 5 °C and 50 °C, although other methods of evaporation, such as freeze drying, microwave drying, vacuum drying or combinations thereof can also be applied.

The evaporation process may be carried out in less than 1 hour, though preferably at least 1 hour, more preferably at least 5 hours. Of course, the resulting material can be subjected to higher temperatures at the beginning or at the end of the evaporation process, e.g. to eliminate any small water traces in a stove at 80 °C or higher.

Milling can be carried out by means of a wide variety of size reduction equipment such as a mortar, a Janke & Kunkel Analysen Mühle A-10 at 20.000 rpm (rounds per minute), a ball-mill or a colloid mill. As desired, the material can subsequently be sieved to the required particle size. The temperature during milling should preferably be kept below the melting point of the material in order to avoid plasticising.

The dye can be added during the process as solution or dispersion in water. A preferred method of preparation is to dissolve or disperse the dye in the water and use the solution or dispersion for the preparation of the biopolymer.

The dye can be added at several stages during the biopolymer preparation process, i.e. before, during or after the evaporation step. If the dye is however thermally unstable, it is preferably added to the biopolymer after the heating step, during the cooling step or during the evaporation process. Another preferred method involves the agglomeration of particles of biopolymer that have been prepared by glueing them together using a dye solution as binder.

Particles comprising the biopolymer material with the associated dye can also be used as coating for a core material, e.g. with the purpose to mask the colour of the core material.

Other methods of preparing the dispersed particle are rolling the carrier material in a bed containing the dye material, or spraying the dye material on the carrier material.

Bleach, builder, clay, abrasive and enzyme can also be used as carrier material and are described hereunder.

Preferably, the level of carrier material is at least 50% by weight of the dispersed particle, more preferably 60% by weight of the dispersed particle, most preferably at least 70% by weight of the dispersed particle. Preferably the level of the carrier material is at most 99.9999% by weight of the dispersed particle, more preferably at most 99.999% by weight of the dispersed particle, most preferably 99.99% by weight of the dispersed particle.

#### NON-AQUEOUS BASE

Non-aqueous liquid cleaning compositions according to the invention comprise a non-aqueous base, i.e. the composition without the carrier-dye material. This base comprises the non-aqueous liquid phase and may comprise a solid phase additional to the dispersed particles of carrier and dye material.

The non-aqueous liquid phase may comprise as liquid material surfactant material, solvent material, non-surfactant material, liquid bleach precursors, deflocculant material other liquid material and mixtures thereof. The non-aqueous liquid phase is present in levels of from 10% to 90%, more preferably from 20%

to 80% and most preferably from 30% to 65% by weight of the non-aqueous base.

This base may optionally comprise a solid phase additional to the dispersed particles of carrier and dye material. In such a case, the solid phase may preferably be from 10% to 90%, more preferably from 20% to 80% and most preferably from 30% to 65% by weight of the non-aqueous base. Such solid dispersed phases may include e.g. one or more components selected from bleach materials, solid bleach activators, builders, abrasives, enzymes, solid surfactant material, minor ingredients such as fluorescers, other solid materials and mixtures thereof.

Usually the particle size of the solid phase in terms of D(3,2) will be less than 100  $\mu\text{m}$ , preferably not more than 30  $\mu\text{m}$ , more preferably up to 10  $\mu\text{m}$  and more than 0.1  $\mu\text{m}$ , preferably from 1  $\mu\text{m}$  and, most preferably, from 2.5  $\mu\text{m}$ . For the purposes of the present invention references to the D(3,2) average particle diameter refer to the D(3,2) particle size, which is an average surface weighted, volume/weight mean diameter determined as described by M Alderliesten, Anal., Proc. Vol. 21, May 1984, 167-172. The particle size can for example, and preferably, be determined using a Malvern Mastersizer.

Preferably the base has a white colour.

As indicated above, the L, A and/or B values of the non-aqueous liquid base are compared with the values of the dispersed particles comprising carrier and dye material whereafter the difference between these values is determined (delta value). It is noted that to increase the delta value, the colour of the non-aqueous liquid base can also be changed. This can e.g. be done for a white coloured base by adding  $\text{TiO}_2$  or a similar whitening agent.

## SURFACTANTS

As explained hereinbefore the liquid phase of non-aqueous liquid detergent compositions often and preferably comprises a liquid nonionic surfactant as major component. Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilising polyalkoxylene or a mono- or dialkanolamide group in chemical combination with an organic hydrophobic group derived from, for example, alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 2 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkylol group having from 1 to 3 carbon atoms are also common. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

In all polyalkoxylene containing surfactants, the polyalkoxylene moiety usually consists of an average of from 2 to 20 groups of ethylene oxide, propylene oxide groups or mixtures thereof. The latter class includes those described in European Patent Specification EP-A-225 654, especially for use as all or part of the liquid phase.

Especially preferred are those ethoxylated nonionics which are condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with 3 to 7 moles of ethylene oxide. Examples of those are the condensation products of C11-13 alcohols with 3 or 7 moles of ethylene oxide. These may be used as the sole nonionic surfactant or in combination with those described in EP-A-225 654.

Another class of suitable nonionics include the alkyl saccharides (polyglycosides/oligosaccharides) and, in particular those described in the following patent specifications, US 3 640 998; US 3 346 558; US 4 223 129; EP-A92 355; EP-A-99 183; EP-A-70 074; EP-A-70 075; EP-A-70 075; EP-A-70 076; EP-A-70 077; EP-A-75 994; EP-A-75 995 and EP-A-75 996.

Mixtures of different nonionic detergent surfactants may also be used. Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or ampholytic surfactants and soaps may also be used.

Preferably the level of nonionic surfactant is from 10 to 90% by weight of the composition, more preferably from 20 to 70% by weight of the composition and, most preferably, from 35 to 50% by weight of the composition.

While nonionic surfactants are quite effective at removing oily and greasy stains, particulate soils such as clay soils may be more effectively removed by anionic surfactants. It may, therefore, be useful to use a combination of different surfactants.

Typical blends of surfactants include a nonionic and/or non-alkoxylated anionic and/or alkoxylated anionic surfactant. Cationic, zwitterionic and amphoteric surfactants may also be present in minor amounts as desired. These and other surfactants are described in "Surface Active Agents" Vol I, by Schwartz &

Perry, Interscience 1949 and "Surface Active Agents" Vol II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in "Tensid \_Taschenbuch", H Stache, 2nd Edn., Carl Hanser Verlag, Munchen & Wien.

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#### OTHER LIQUID MATERIAL

Other liquid material which may be present in the liquid phase include liquid bleach precursors such as for example glyceroltriacetate, solvent material, for example ethanol and dodecanol, and deflocculant material such as described in EP 266199. The level of liquid precursors is preferably 0 to 20% by weight, more preferably 1 to 25 % by weight and, most preferably 2 to 10% by weight. The level of solvents, other than nonionic surfactants, is preferably from 0 to 20% by weight, most preferably 0 to 15% and most preferably 0 to 10%.

In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-266 199 (Unilever). The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

Deflocculants are preferably selected from Bronsted acids and Lewis acids. Examples thereof are transition metals, anhydrides, organic acids, inorganic mineral acids and salts,  $C_8$ - $C_{20}$  fatty acids and salts,  $C_1$ - $C_{10}$  alkanolic acids, substituted anhydrous alkali-metal aluminosilicate, alkyl, alkenyl aryl, aralkyl and aralkenyl sulphonic or carboxylic acids and salts and halogenated derivatives thereof, zwitterionic surfactants, anionic surfactants of the formula R-L-A-Y as defined in EP 266199 and compounds having an acidic P-OH group. Preferably, deflocculants in the acid form are used.

Deflocculant material, if included, may be present at levels of from 0 to 15%, preferably at least 0.01 and most preferably at least 1% by weight. For most purposes, the amount of deflocculant material will be from 2 to 12 % by weight, preferably 4 to 10% by weight based on the final composition.

#### BLEACH SYSTEM

Suitable bleaches for inclusion in the detergent compositions of the invention include halogen, particularly chlorine bleaches such as are provided in the form of alkali-metal hypohalites, eg hypochlorites. When the compositions of the invention are to be used for fabric washing, oxygen bleaches are preferred, for example, in the form of an inorganic persalt, preferably with a bleach precursor, or as a peroxy acid compound.

In the case of inorganic persalt bleaches, an activator or bleach precursor makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60 °C. Such bleach systems are commonly known as low-temperature bleach systems. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator which is usually an organic compound having one or more reactive acyl residues which causes the formation of peroxy acids; the latter providing for more effective bleaching action at lower temperatures than the peroxybleach compound alone. A commonly used precursor is tetraacetyl ethylene diamine (TAED).

The ratio of the peroxybleach compound to the activator is from 20:1 to about 1:1, preferably from about 10:1 to about 1.5:1. The preferred level of the peroxybleach compound in the composition is from 0 to 30, more preferably 2 to 20 and most preferably 4 to 15% by weight. The preferred level of activator is from 0 to 20, more preferably 1 to 10, most preferably 2 to 8% by weight of the composition.

Typical examples of suitable peroxybleach compounds are alkali-metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate and sodium percarbonate are preferred.

A further class of bleach activators are hydrophobic peroxy acid bleach precursors such as sodium nonanoyl benzene sulphonate and sodium-3,5,5-trimethyl hexanoyloxy benzene sulphonate.

It is also advantageous to include bleach catalysts and, in particular, transition metal catalysts. Such catalyst, optionally together with stabilisers, as hereinafter defined, can be used to activate peroxide compounds to make them more suitable for use for bleaching at lower temperatures, ie from 20-60 °C. As stated above, such catalysts may be incorporated in the form of a particulate product according to the invention. A particularly suitable bleach catalyst usable herein in combination with an oxygen bleach in the form of an inorganic persalt with or without a bleach precursor or as a peroxyacid compound, is a dinuclear manganese (III) - or Manganese (IV) complex as described in EP 458397 and EP 458398. Preferred catalysts of this class are those referred to as having the following formulae:

- 1)  $[\text{Mn}^{\text{IV}}_2(\text{m-O})_3(\text{Me-TACN})_2](\text{PF}_6)_2$
- 2)  $[\text{Mn}^{\text{IV}}_2(\text{m-O})_3(\text{Me/Me-TACN})_2](\text{PF}_6)_2$
- 3)  $[\text{Mn}^{\text{III}}_2(\text{m-O})(\text{m-OAc})_2(\text{Me-TACN})_2](\text{PF}_6)_2$
- 4)  $[\text{Mn}^{\text{III}}_2(\text{m-O})(\text{m-OAc})_2(\text{Me/Me-TACN})_2](\text{PF}_6)_2$

Wherein Me-TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane, and Me/Me-TACN is 1,2,4,7-tetramethyl-1,4,7-triazacyclononane.

These catalysts may be used in the present invention in an amount corresponding to a Manganese level of from about 0.0001 to about 1.0% by weight, preferably from about 0.0005 to about 0.5% by weight.

It may also be desirable to include in the compositions a stabiliser for the bleach or bleach system, for example hydroxyethylidene-1,1-diphosphonic acid, ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonates or salts thereof, such as the Dequest® range of materials.

#### DETERGENCY BUILDERS

The detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders.

They may also be sub-divided into the phosphorus-containing and non-phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various phosphate-, carbonate-, silicate-, borate- and aluminosilicates-type materials, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates such as sodium metasilicate and zeolites.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the tradename of the Dequest® range and alkanedihydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co-polymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/polymaleic acid co-polymers and their salts, such as those sold by BASF under the Sokalan® Trade Mark. Polyacrylates or their derivatives may also be useful for their anti-ashing properties.

Preferably the level of builder materials is from 5-50% by weight of the composition, more preferably 10-40%, most preferably 15-35%.

#### HYDROPHOBICALLY MODIFIED MATERIALS

The physical stability of non-aqueous liquid detergent compositions can be improved and/or setting problems can be minimised, if hydrophobically modified dispersants (hereinafter termed HM materials) are used.

For the purpose of the present invention, a dispersant material is a material, of which the main purpose is to stabilise the composition. Hydrophobically modified dispersant materials are particulate materials, of which the outer surface has chemically been treated to reduce the hydrophilic nature thereof.



Preferred HM materials have a D(3,2) weight average particle size of from 0.005 to 5 micrometers, more preferred 0.01 to 3 micrometers, most preferred from 0.02 to 0.5 micrometer. The amount of the HM material is preferably from 0.1 to 10 % by weight of the composition, more preferred 0.3 to 5 %, most preferred from 1.0 to 4 %.

5 Preferably the number of hydroxy- and/or acid- groups at the surface of the particles is reduced by the hydrophobic modification treatment. Suitable reactions include esterification or etherification of the hydrophilic groups. Preferably the hydrophobic modification treatment involves at least 10 % of the hydrophilic groups at the surface of the particle, more preferably from 40 to 95 %, most preferably from 50 to 90 %. Partial hydrophobing is preferred over complete hydrophobic modification.

10 Preferably HM silica containing dispersants are used. The hydrophobic modification of the silica particles preferably involves the substitution of the free hydroxy-groups at the outer surface of the silica particles by a short alkyl or silyl group. More preferably the surface hydroxy-groups are substituted by methyl groups.

For even greater reduction the clear layer separation of liquid detergent compositions of the invention, it has been found that the use of particulate metal oxides is especially advantageous. Preferred suspended metal oxides have a bulk density of 200 to 1,000 g/l, more preferred 250 to 800 g/l, especially preferably 300 to 700 g/l, most preferably from 400 to 650 g/l.

Preferably, the metal oxide is selected from calcium oxide, magnesium oxide, silicon dioxide and aluminium oxide, most preferably magnesium oxide is used.

20 The weight average particle size of the metal oxide is preferably from 0.1 to 200 micrometers, more preferably from 0.5 to 100 micrometers, most preferably from 2 to 70 micrometers. The level of metal oxide is preferably from 0.1 to 7 % by weight of the composition, more preferably from 0.5 to 5 %, most preferably from 1 to 4 %.

Appropriate clays may also be incorporated to fulfil this purpose and/or for fabric softening.

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#### OTHER OPTIONAL INGREDIENTS

Other ingredients comprise those remaining ingredients which may be used in liquid cleaning products, such as fabric conditioning agents, abrasive material, enzymes, enzyme stabilising agents, fluorescer, 30 perfumes (including deoperfumes), micro-biocides, soil-suspending agents (anti-redeposition agent), corrosion inhibitors, and lather depressants.

Amongst the fabric conditioning agents which may be used, either in fabric washing liquids or in rinse conditioners, are fabric softening materials such as fabric softening clays, quaternary ammonium salts, imidazolium salts, fatty amines and cellulases. Fabric softening clays are usually phyllosilicate clays with a 2:1 layer structure, which definition includes pyrophyllite clays, smectite or montmorillonite clays, saponites, 35 vermiculites and micas. Preferably the clay is selected from Montmorillonite, Saponite clays and mixtures thereof. More preferred are smectite clays described in detail in US 3,959,155 and US 3,936,537. Other suitable clays are disclosed in EP 26,528

Abrasive are particularly preferred for incorporation in hard surface cleaners (liquid abrasive cleaners). 40 These will inevitably be incorporated as particulate solid. They may be those of the kind which are water insoluble, for example calcite. Suitable materials of this kind are disclosed in the applicants' patent specifications EP 50887, EP 80221, EP 140452, EP 214540 and EP 9942, which relate to such abrasives when suspended in aqueous media. The abrasives may also be water soluble, especially in the form of particles of any solid water soluble salt hereinafter described, for example as an inorganic builder. Inert 45 particulate solid salts having no particular function in fabric washing, other than as bulking agents in detergent powders, e.g. sodium sulphate may also be used for this purpose. Especially preferred are the water soluble abrasives described in the applicants' patent specification EP 193,375.

Enzymes which can be used in liquids according to the present invention include proteolytic enzymes (protease), amylolytic enzymes (amylase), lipolytic enzymes (lipases) and cellulolytic enzymes (cellulase). 50 Various types of proteolytic enzymes and amylolytic enzymes are known in the art and are commercially available. They may be incorporated as "prills", "marumes" or suspensions. Preferably enzymes are added as suspensions in a non-aqueous liquid surfactant. The preferred level of enzyme materials is from 0.01 to 5% by weight of the composition.

The total amount of the fluorescent agent or agents used in a detergent composition is generally from 55 0.02-2% by weight.

When it is desired to include anti-redeposition agents in the liquid cleaning products, the amount thereof is normally from about 0.1% to about 5% by weight, preferably from about 0.2% to about 2.5% by weight of the total liquid composition. Preferred anti-redeposition agents include carboxy derivatives of sugars and

celluloses, e.g. sodium carboxymethyl cellulose, anionic poly-electrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

## USE

Composition in accordance with the present invention may be used for several detergency purposes, for example the cleaning of surfaces and the washing of fabrics. For the washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2%, of the non-aqueous detergent composition of the invention is used.

## PROCESSING

During manufacture of the non-aqueous liquid, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids. In order to minimise the rate of sedimentation of the solids, this blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of de-aeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled in the art.

It follows that all equipment used in this process should preferably be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

The particles comprising carrier material and dye material associated thereto, according to the invention, can be prepared separately, as discussed above, whereafter they are dispersed in the non-aqueous phase of the non-aqueous cleaning product, e.g. by mixing using high shear or using a mill. Preferably, the D(3,2) particle size is of from 0.1  $\mu\text{m}$  to 2000  $\mu\text{m}$  in the non-aqueous phase.

The invention will now be illustrated with respect to the following non-limiting examples.

**EXAMPLE 1**

A non-aqueous liquid was prepared by adding the following ingredients in the order listed.

INGREDIENTS	% BY WEIGHT
Nonionic 1)	16.1
Nonionic 2)	19.7
Propyleneglycoldiacetate	10.0
Marlon AS-3 (3)	6.0
Na. Carbonate	20.0
Ca. Carbonate	6.0
Polymer (4)	3.0
Sipernat D17 (5)	3.0
Na. Perborate monohydrate	10.5
Biopolymer (6)	2.5
Minors	ad 100.0

1) Vista 1012-62

2) Dobanol 25-3

3) Anionic detergent in acid form ex Huls

4) Versa T1-3; copolymer of sulphonated styrene and maleic anhydride, Na salt, ex National Starch & Chemical Co.

5) Hydrophobically modified silica dispersant ex Degussa

6) The biopolymer material was starch and it contained 0.35% pigment paste (Dispersed Blue 69-0007 ex BASF); the D(3,2) particle size was 150 $\mu$ m; it had a density of 1.3 and was prepared by solubilising starch with water and adding solutions of the bleach catalyst and paste.

The dispersed particles of carrier material and dye material had an excellent appearance in the non-aqueous base and the L, A as well as the B values showed a difference of more than 20 units, also after storage for 4 weeks at 37 °C.

**EXAMPLE 2**

Particles of starch were prepared as in Example 1. The following distribution was obtained.

Particle size distribution:	
>500 $\mu$ m	0 wt%
>425 $\mu$ m	0.1 wt%
>355 $\mu$ m	0.2 wt%
>300 $\mu$ m	0.4 wt%
from 90 to 300 $\mu$ m	87.6 wt%
<90 $\mu$ m	10.1 wt%
<53 $\mu$ m	1.6 wt%

The particles were distributed in a non-aqueous liquid of the following composition:

# EP 0 635 569 A2

INGREDIENTS	% BY WEIGHT
Nonionic 1)	21.91
Nonionic 2)	17.94
Solvent material	10.00
LAS acid	6.00
Solid Builder Material	24.00
Polymer	1.50
Hydrophobed silica	3.00
Perborate monohydrate	10.50
Minors	5.15

- 1) Vista 1012-62  
2) Dobanol 25-3

Even after storage of 2 months at room temperature, the dispersed particles of carrier material and dye material had a good appearance in the non-aqueous base and the L, A as well as the B values showed a difference of more than 20 units.

## EXAMPLE 3

Similar results as in Example 2 were obtained with the starch particles with the following particle size distribution in a non-aqueous liquid with the same composition:

>500 $\mu\text{m}$	0 wt%
>425 $\mu\text{m}$	0 wt%
>355 $\mu\text{m}$	0 wt%
>300 $\mu\text{m}$	0.1 wt%
from 90 to 300 $\mu\text{m}$	75.0 wt%
<90 $\mu\text{m}$	22.9 wt%
<53 $\mu\text{m}$	2.0 wt%

## EXAMPLE 4

Similar results as in Example 2 were obtained with the starch particles with the following particle size distribution in a non-aqueous liquid with the same composition:

>500 $\mu\text{m}$	0 wt%
>425 $\mu\text{m}$	0 wt%
>355 $\mu\text{m}$	0 wt%
>300 $\mu\text{m}$	0 wt%
from 90 to 300 $\mu\text{m}$	78.7 wt%
<90 $\mu\text{m}$	19.4 wt%
<53 $\mu\text{m}$	1.9 wt%

## EXAMPLE 5

Two non-aqueous liquids were prepared with nonionics and bleach/builder particles, similar to the composition of Example 2. To liquid 1, starch particles per se with a size according to the invention were added (colour of the starch is light brown; the colour of the base is white) and to liquid 2, starch particles were added that were dyed blue (colour of the starch is blue; the colour of the base is white). Overall, 47 panellists judged Liquid 2 to have a better appearance than Liquid 1.

Claims

1. A non-aqueous liquid cleaning composition comprising a non-aqueous liquid phase with dispersed particles comprising a carrier material and dye material associated thereto wherein the particles have a D(3,2) particle size of from 50 $\mu$ m to less than 500 $\mu$ m.
2. Composition according to claim 1, wherein the volume fraction of dispersed particles in the non-aqueous phase is from 0.1 to 5.0% V/V.
3. Composition according to claims 1-2, wherein the difference between the L, A and/or B colour intensity value of the dispersed particles with carrier and dye material and the value of the non-aqueous base is higher than 10 and/or lower than -10.
4. Composition according to claims 1-3, wherein the dispersed particles comprising the carrier material and dye material have density of from 0.1 to 1.5 g/ml.
5. Composition according to claims 1-4, wherein the carrier material comprises a biopolymer material.
6. Composition according to claims 1-5, wherein the dispersed particle of carrier material and dye material is present in amounts of from 0.01 to 80% by weight of the composition.
7. Composition according to claims 1-6, wherein 0.0001 to 5% by weight of the dispersed particle of dye material is present.
8. Composition according to claims 1-7, wherein the composition further comprises a bleach system.
9. Method of preparing a non-aqueous liquid cleaning composition according to claims 1-8, said method comprising dispersing of particles comprising carrier material and dye material associated thereto, in the non-aqueous phase.
10. Method of preparing a particle, comprising carrier material and dye material associated thereto, and suitable for use in a non-aqueous liquid cleaning composition, said method comprising dissolving of biopolymer material in water, evaporating the water to an amount of lower than 15% by weight of the resulting material and before, during or after the evaporation step, adding of dye material.